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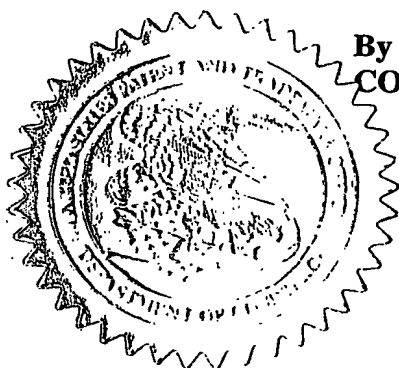
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M. SIAS
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR §1.53(c).

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
Yet-Ming John B.		Chiang Vander Sande		Framingham, MA Newbury, MA	
<input type="checkbox"/> Additional inventors are being named on the <u>0</u> separately numbered sheets attached hereto.					
TITLE OF THE INVENTION (280 characters max)					
Fullerene Particles and Composite Fullerene Particles and Process of Manufacture					
CORRESPONDENCE ADDRESS					
Direct all correspondence to:					
<input type="checkbox"/> Customer Number:		<div style="border: 1px solid black; padding: 5px; display: inline-block;"> Place Customer Number Bar Code Label Here </div>			
OR					
<input checked="" type="checkbox"/> Firm or Individual Name		Eric L. Prah Fish & Richardson P.C.			
Address		225 Franklin Street Boston, MA 02110-2804			
Country		United States	Telephone	(202) 783-5070	Fax (202) 783-2331
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification	Number of Pages	24	<input type="checkbox"/> CD(S), Number		
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input checked="" type="checkbox"/> Other (specify)	Cover Sheet (1 page)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76.					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)					
<input checked="" type="checkbox"/> Applicant Claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
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<input type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:				06-1050	
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<input type="checkbox"/> No.					
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:					
Office or Naval Research Grant No. N000014-98-1-354					

Respectfully submitted,


Signature

Name Harold H. Fox, Reg. No. 41,498

Date April 9, 2002

Telephone No. (202) 783-5070

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FULLERENIC PARTICLES AND COMPOSITE FULLERENIC PARTICLES AND PROCESS OF MANUFACTURE

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The U.S. Government may have certain rights in this invention pursuant to Grant No. N000014-98-1-0354 awarded by the Office of Naval Research.

TECHNICAL FIELD

5 This invention relates to compositions including fullerenic particles and methods of preparing fullerenic particles.

BACKGROUND

Carbon can adopt a fullerene-like structure, or fullerenic structure, such as in a C60 or C70 fullerene or a carbon nanotube. A carbon nanotube can have a helical tubular structure and can have a single wall or multiple substantially concentric walls. Carbon nanotubes can have diameters ranging between a few nanometers to a few hundred nanometers. Carbon nanotubes can be conductors or semiconductors. The unique structure of the nanotubes can provide good mechanical, electrical and chemical properties. The high aspect ratio of carbon nanotubes can provide high strengths, for example, a high specific modulus (Young's modulus ~1 TPa) and tensile strength (~60 GPa). The electrical and chemical properties of the nanotubes can be suitable for hydrogen and lithium storage for electrochemical energy sources such as fuel cells and lithium batteries. Previous methods of preparing carbon nanotubes include arc-discharge, chemical vapor deposition, and flame processes.

SUMMARY

20 In one aspect, a composite includes a particle including a core and a shell covering at least a portion of a surface of the core including fullerenic carbon. The core includes silicon carbide.

25 The shell can cover at least 50%, 65%, 80%, 90%, or 95% of the surface. The particle can include at least 2%, 5%, 10%, 15%, 25%, 50%, 75%, 90% or 95% by volume fullerenic carbon. The shell can have an average thickness of at least 2.5, 5, 10, 25, 50 or 100 nm. The particle can have an average diameter of less than 100, 50, 20, 10, 5, 2.5, 1.0, 0.5, 0.25, or 0.1 micrometers.

In another aspect, a composite particle includes a silicon carbide core and a fullerenic outer shell.

In another aspect, a particle includes substantially densely-packed fullerenic carbon. The particle can include a coating of metal oxide or metal over the fullerenic carbon or a metal oxide or metal infiltrating the fullerenic carbon.

In another aspect, a grinding or finishing product including the abrasive particle. The grinding or finishing product can be a grinding wheel, cutting wheel, coated abrasive, or suspension of abrasive particles in a liquid.

The fullerenic carbon can be a single-walled carbon nanotube, a multi-walled carbon nanotube, or a nanofiber. The fullerenic carbon can be chemically attached to the core of silicon carbide, for example, by at least one end of the nanotube or nanofiber. The fullerenic carbon can include a carbon nanotube or carbon nanofiber being open at an end not attached to the core.

In another aspect, a method of manufacturing an article including fullerenic carbon on a surface of the article includes heating the article including a metal carbide in a first atmosphere for a period of time to generate fullerenic carbon nuclei on the surface of the article, the first atmosphere being a reducing atmosphere relative to the metal carbide, and heating the article including fullerenic carbon nuclei in a second atmosphere to grow the fullerenic carbon on the surface of the article. The metal carbide can include silicon carbide. The silicon carbide can be cubic or beta silicon carbide powder, or hexagonal or alpha silicon carbide powder. The method can include providing a carbon source for growing the fullerenic carbon. The carbon source can be a material other than silicon carbide. Heating the article including the metal carbide in the first atmosphere can include heating the article at a pressure of greater than 10^{-3} Torr (e.g., greater than 10^{-2} Torr, greater than 10^{-1} Torr, greater than 1 Torr, greater than 10 Torr or at atmospheric pressure) at a temperature between 1200°C and 2000°C. The article can be a powder.

In another aspect, a method of manufacturing fullerenic carbon includes heating silicon carbide in an oxygen-containing gas atmosphere and at a temperature in which silicon carbide is in the active oxidation regime and carbon is in the graphite stability regime. The gas and temperature can be selected based on accepted thermochemical data. The gas atmosphere supplied to the silicon carbide can be CO or a mixture of CO and CO₂. The temperature can be in the range 1000°C to 2000°C.

In another aspect, a method of manufacturing fullerenic carbon includes heating silicon carbide in an inert gas atmosphere at a temperature between 1200°C and 2000°C. The inert gas can include helium, hydrogen, a nitrogen-hydrogen mixture, or argon. The method can include heating the silicon carbide to nucleate the fullerenic carbon prior to heating the silicon carbide in an inert gas atmosphere at a temperature between 1200°C and 2000°C.

Previous methods of preparing carbon nanotubes such as arc-discharge, chemical vapor deposition, and flame processes result in highly dispersed fullerenes and carbon nanotubes of low packing density. This is a disadvantage for many applications where a high volume fraction of fullerenes in the final product is desired. Furthermore, fullerenes produced by arc-discharge or chemical vapor deposition are expensive materials currently selling for thousands of dollars per pound. In order to realize widespread application of carbon nanotubes, economical processes and starting materials are necessary. The method of manufacturing fullerenic carbon can be used to produce large volumes of relatively dense fullerenic carbon at a lower per pound cost than previous methods.

The details of one or more embodiments are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

FIGS. 1A and 1B are photographs depicting electron microscope images of fullerenic carbon composite particles.

FIG. 2 is a pair of photographs depicting SiC powder and SiC powder converted to carbon nanotubes.

FIGS. 3A and 3B are photographs depicting electron microscope images of fullerenic carbon prepared from SiC particles.

FIG. 4 is a graph depicting the charge-discharge characteristics of SiC-derived carbon nanotubes at 60 mA/g.

FIG. 5 is a graph depicting the capacity versus cycle number for SiC-derived carbon nanotubes at a current rate of 20 mA/g and 60 mA/g.

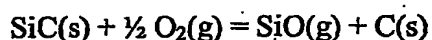
DETAILED DESCRIPTION

Fullerene particles and composite fullerene particles, and various applications of such particles including but not limited to structurally reinforced composites in which particles are contained within a matrix, can be used as electrochemical storage media and devices using such media, abrasives, and polishing compounds. Fullerene particles and composite fullerene particles can be particles composed of an aggregate of single-walled or multiwalled carbon nanotubes that are compact or densely packed compared to previously produced forms of carbon nanotubes.

The composite particles can have an outer shell of fullerene carbon which is attached to an underlying core of a material that is not fullerene carbon. Such a composite fullerene particle provides new functionality not achievable with dispersed fullerenes. According to the invention they can have a wide range of fullerene fraction ranging from a thin surface layer of fullerene "caps" (e.g., a segment of a C60 sphere) on an underlying substrate material, to a particle which can be entirely comprised of fullerene material. The mean final particle size of the particles can be between 0.1 and 100 micrometers (or between 0.1 and 20 micrometers), wherein 50% to 100% of the external surface area consists of fullerene carbon. The volume fraction of the particles occupied by fullerene carbon can range from a few volume percent, corresponding to a thin surface shell, to 100%. The fullerene carbon can include segments of fullerene molecules such as C60 and C70, single walled carbon nanotubes, or multiwalled carbon nanotubes.

Methods for growing the fullerene carbon from a core of silicon carbide can include a number of variations. In the first of these methods, the nucleation of carbon nanotubes can be allowed to occur by providing a starting SiC that has a thin surface oxide layer, or by heating the SiC initially in an atmosphere containing sufficient oxygen to allow surface oxidation. This nucleation or seeding step can be followed by heating the material under thermochemical conditions that allow continued growth of the nucleated carbon nanotubes. The nucleation and growth processes can be carried out in a continuous manner (i.e., within the same heat treatment cycle), or the heat treatment can be interrupted after the nucleation step and a separate growth heat treatment conducted later. When a large fraction of fullerene carbon is desired or when large silicon carbide particles are employed, it can be especially advantageous to carry out the growth step under conditions that give maximum growth rates of the carbon nanotubes. One such growth condition includes heating the

material in a carbon monoxide/carbon dioxide (CO/CO₂) gaseous atmosphere in which active oxidation of SiC, represented by the reaction



is thermodynamically favored in the forward direction. The sample can be open to the firing atmosphere so that the SiO can volatilize, lowering the SiO activity in the vicinity of the sample, and the oxygen necessary to sustain the reaction is provided by the CO/CO₂ gas mixture. The oxidation reaction can be carried out at temperatures and under gas atmospheres where the graphitic form of carbon is stable as a solid phase. This ensures that the growing carbon nanotubes are not themselves oxidized to CO or CO₂. The rate of conversion of the silicon carbide to carbon nanotubes can be maximized by electing thermochemical conditions where the SiO vapor pressure is maximized and conducting the process in an open or convective gas atmosphere such that the transport of SiO gas away from the particles is improved. The temperatures and gas mixtures necessary to accomplish these objectives are readily determined from available thermochemical data.

A second method includes nucleation or growth processes in which the direct volatilization of Si as a vapor allows growth of the carbon nanotubes via the reaction



In this instance, no oxygen source is necessary. The gas atmosphere used can be at a reduced pressure, such as a pressure greater than 10⁻³ Torr, or can be an inert gas such as argon, helium, hydrogen, or nitrogen-hydrogen mixtures. A mixture of a reactive gas and an inert gas can also be used, and one or both of the two mechanisms of growth can be carried out in a given heat treatment.

Another method of fabricating the composite particles can include growing fullerenes from an external source of carbon on a particle of silicon carbide or a fullerenic particle derived from silicon carbide. The source of carbon can be a gas phase reactant as is used in the chemical vapor deposition or flame synthesis of fullerenes.

The fullerenic materials can be subsequently treated to improve their properties for specific applications. Such methods include chemical or thermochemical/oxidation treatments that open the ends of the carbon nanotubes, allowing better penetration by hydrogen or lithium, or coating the carbon nanotubes with another material to improve wetting or bonding. Another method of improving electrochemical storage capacity is the

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process of first coating or filling the carbon nanotubes with a metal oxide, then reducing the metal oxide chemically or thermochemically to its metal, after which the metal can reversibly alloy with lithium or hydrogen without capacity loss, due to the accommodation of the volume expansion of alloying provided by having shrinkage during the reduction step.

5 A powder can include particles having a surface including predominantly fullerenic "caps" or open tubes, formed by carrying out one of the above processes to produce fullerenes on a substrate, and subsequently removing or dissolving the substrate to leave behind the open fullerenes.

10 A manufacturing processes for the fullerenic carbon or composite particles can include: (1) a continuous conveyer system is used to carry the starting silicon carbide powder through a furnace or series of furnaces in which thermochemical conditions are controlled to effect nucleation and growth of carbon nanotubes as described above, at the end of which a continuous supply of fullerenic or composite powder is delivered; or (2) a fluidized-bed reactor is used to continuously stir a bed of silicon carbide powder using one of the above mentioned gases while heating to maintain the desired thermochemical conditions. 15 In this process, convection increases the carbon nanotube conversion rate and uniformity within the powder bed.

20 Silicon carbide powder can be partially or completely converted to substantially densely-packed carbon nanotubes by thermochemical treatment. When partially converted, the resulting materials consist of a silicon carbide core onto which a surface layer of carbon nanotubes has been grown. The carbon nanotubes can be grown so that they are substantially parallel and have their axes oriented outwards from the particle surface, with the interior end of the nanotubes bonded to the silicon carbide core. In addition, the nature of the fullerenic material and its orientation or texture can be varied should such variations prove important in enhancing properties and performance of the particle. The fraction of the particle that is 25 silicon carbide and that is fullerenic can be controlled by the heat treatment atmosphere, time, and temperature. When fully converted, particles consisting of densely-packed carbon nanotubes can be obtained.

30 Abrasives and polishing compounds for grinding and finishing can include fullerenic carbon produced from partially or completely converted from silicon carbide. Grinding and cutting wheels, coated abrasives, and suspensions in liquid media including the fullerenic

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carbon or composites can be used for cutting or polishing. The fullerenic carbon can be modified such that the ends of the nanotubes can be opened by chemical (e.g., acid) or thermochemical/oxidation treatments, or the fullerenic carbon can be coated or infiltrated with a metal oxide or metal.

5 Fullerene-Containing Composites. Carbon nanotubes have enormous tensile strength and elastic modulus, but being composed of closed graphene sheets, are known to chemically bond to only a limited number of materials. However, when a multiplicity of carbon nanotubes are grafted to an underlying silicon carbide particle, the resulting composite particle is an entity of high strength which has a "brushy" exterior which is more easily
10 functionalized or bonded to. See, for example, FIG. 1A or FIG. 3A. The fullerenic or composite particles can be useful as reinforcing additives in a broad range of composite materials. Specific applications including use as reinforcements in filled polymers and rubber tires, in the latter case replacing some or all of the currently used carbon black fillers. Performance advantages of a fullerene-filled polymeric or elastomeric composite compared to one made with conventional fillers include higher strength, fracture toughness, elastic modulus, thermal conductivity, and wear resistance.

15 The materials can be used as reinforcements in metal-matrix or ceramic-matrix composites in which the superior mechanical properties of carbon nanotubes can be useful. Suitable dispersion and wetting of the fullerenic carbon can be achieved by dispersion/wetting of carbon nanotubes using metal oxides formed from aqueous solutions (i.e., sol-gel approach) or reduction of the wetted metal oxide to its metal, allowing subsequent alloying with common structural metals, for example, aluminum. Several metal oxides can be produced from solution, including V_2O_3 , PbO_x , and BiO_x which can wet carbon nanotubes. See, for example, T.W. Ebbesen, Physics Today, p. 26, June 1996 and
25 P.M. Ajayan *et al.*, Nature 375:564 (1995) and 361:333 (1993), each of which is incorporated by reference in its entirety. Weak van der Waals forces causing a dense-packed array of carbon nanotubes to remain aggregated can be overcome by wetting and penetration by the metal oxide. The metal oxide coating can be selected to be one that is thermochemically reduced by a matrix alloy, such as aluminum. Upon reduction of the coating to its metal, alloying and penetration by the aluminum matrix is expected.

30 Other transition metal oxides can also wet the fullerenic carbon. Metals can be selected base on the ease of reduction and the utility of the metal as an alloying additive.

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Metals with less negative free energy of oxidation, namely those towards the top of the Ellingham diagram, are of greatest interest. In particular, the oxides of Cu, Sn, Zn, Fe, Ni, Co, Pb and Ag can be suitable. Of these, the oxides of Cu, Sn, Zn, and Ag can be especially easy to reduce at low temperatures. The oxides of Cu and Zn are of particular interest since they are components of 6000 and 7000 series aluminum alloys, respectively.

Electrochemical Energy Storage. High electrochemical storage capacity for lithium and hydrogen on a weight basis (gravimetric capacity) has been reported for various carbon nanotubes and carbon nanofibers. See, for example, C. Liu *et al.*, Science, 286:1127 (1999), M. Dresselhaus *et al.*, MRS Bulletin, p. 45, Nov. 1999, D. Frackowiak *et al.*, Carbon, 37:61-69 (1999), G.T. Wu *et al.*, J. Electrochem. Soc., 146(5):1696 (1999), B. Gao *et al.*, Phys. Lett., 307:153 (1999), and A. Chambers *et al.*, J. Phys. Chem. B, 102, 4253 (1998), each of which is incorporated by reference in its entirety. However, while the specific capacity of carbon nanotubes is high, the volumetric capacity is low in comparison with metal hydrides used for fuel cells and nickel-metal-hydride rechargeable batteries, or denser forms of carbons used for anodes in lithium ion batteries. In real devices, volumetric capacity can be as, or more, important than specific capacity. The poor volumetric capacity of carbon nanotubes is due to the fact that they are produced in loose form, and having an exceptionally high elastic modulus (~1 TPa) resists deformation upon compaction. A dense-packed form of fullerenic carbon that can be produced in sufficiently large volumes for meaningful tests can take practical advantage of the high specific capacity.

The Examples contained herein show that silicon carbide powder with a particle size on the order of one micrometer can be completely converted to a substantially dense array of fullerenic carbon nanotubes. Because the particles are on average more than 50% converted to carbon nanotubes, and the particles themselves can be packed to a volumetric density exceeding 50%, this material provides the highest bulk packing density of any form of fullerenic carbon yet achieved. Thus, unlike previous fullerenic materials with very low packing density, these new materials have greater utility as lithium ion, proton, or hydrogen gas storage materials due to the high volumetric density of fullerenic carbon. A higher volumetric packing density allows a higher volumetric energy density for the same material. See FIGS. 2 and 3.

Electrochemical storage devices utilizing this novel material can include but are not limited to lithium batteries, metal hydride batteries, hydrogen storage materials, and fuel cells utilizing such hydrogen storage materials.

Abrasives and Polishing Compounds. There are numerous potential advantages to include the fullerenic carbon in abrasives. The composite nanostructure of the particle, terminating in a "brushy" array of fullerenes, allows improved bonding to matrix or adhesive materials that are used to hold the abrasive particles. See, for example, FIG. 1A or FIG. 3A. These can be polymeric or metallic in nature, and the resulting composite may be a cutting or grinding wheel or a coated abrasive. Improved bonding of the abrasive to the matrix can improve the lifetime and cutting efficiency of the abrasive product. Fullerenic carbon can be mechanically extremely strong and stiff, and are chemically and thermally quite stable solids. Fullerenic carbon can also have at least one very well-defined dimension; in the case of the present process, multiwalled nanotubes of 2-10 nm diameter can be obtained. As an abrasive or polishing compound, the characteristic dimension of the fullerenic carbon in contact with the workpiece is therefore well-defined and highly uniform, and can give improved surface finishes compared to abrasives in which a distribution of particle sizes are in contact with the workpiece. A composite particle of fullerenes grafted to an underlying silicon carbide particle can be very wear-resistant and durable. The overall particle size of the fullerenic or fullerene-terminated abrasive particle is readily controlled, as it is determined by the starting SiC particle size in the present process. Compared to other forms of fullerenic carbon such as those made by arc discharge or laser ablation or chemical vapor deposition, the present material is both much cheaper and has a higher packing density. It is more easily handled, and can be incorporated into grinding and finishing products at a high volumetric density that is not achievable with other forms of fullerenes.

When further modified, the present abrasives acquire additional useful properties. As an example of an application as a chemical-mechanical-polishing (CMP) compound, the fullerenic carbon structures can be coated, or the interior of the carbon nanotubes filled, with a metal oxide such as SiO_2 , Al_2O_3 , or CeO_2 that exhibits chemical-mechanical polishing activity. Combining the oxide with the fullerenic structure allows control of the active particle size, and improves the durability of the polishing compound. Electrochemical activity between the carbon, the oxide, or the work piece can also improve material removal rates or surface finish.

When coated with a metal or metal oxide, the bonding of the abrasive particle to polymeric or metallic matrix materials (e.g., for use as a cutting or grinding wheel) is further improved. In one variant of this concept, wetting of the particles by a metal is improved, allowing dispersion and good bonding of the abrasive to a metal matrix. If the fullerenic abrasive particle is coated by a metal, said metal can then be selected so that it is wet by the matrix metal. In the instance where the fullerenic abrasive particle is coated with a metal oxide, the metal oxide can be selected to be one that is thermochemically reduced to its metal upon contacting the matrix metal. For example, a matrix metal with a more negative free energy of oxidation will reduce a coating metal oxide with less negative free energy of oxidation, allowing infiltration of the matrix metal between the fullerenes and resulting in good bonding. Aluminum, magnesium, and titanium are examples of metals with large negative free energies of oxidation, and which as a matrix material would reduce a coating that is an oxide of such as Cu, Ag, Sn, V, Fe, or Zn, which have less negative free energies of oxidation.

Abrasives and polishing compounds for grinding and finishing can consist of fullerenic carbon that has been partially or completely converted from silicon carbide. The invention also comprises products such as grinding and cutting wheels, coated abrasives, and suspensions of the subject materials in liquid media used for cutting or polishing. The invention also comprises modified forms of the subject fullerenes used in an abrasive or polishing application, such as those in which the ends of the nanotubes have been opened by chemical (e.g., acid) or thermochemical/oxidation treatments, or those that have been coated or filled with a metal oxide or other material.

The following examples relate to the manufacture and use of fullerenic carbon and composite particles.

Example 1

1.696g of a Norton Company Crystolon™ SiC powder with a specific surface area of 15 m²/g was weighed into a high purity graphite crucible and placed in an Astro Industries, Inc. (Santa Barbara, California) graphite resistance-heated high temperature furnace. The furnace was pumped down to primary vacuum using a rotary mechanical pump, and heated to 1700°C and held at that temperature for 4 hours. Upon cooling, a blackish powder was observed on the surface of the sample whereas the powder was beige before heat treatment.

The weight loss of the powder was measured to be 5%, indicating partial conversion of the SiC to carbon overall. (Full conversion has an ideal weight loss of 70%). The black surface powder was removed and studied by high resolution electron microscopy (HREM). Micrographs depicting fullerenic carbon nanotubes on a surface of the silicon carbide particles are shown in FIGS. 1A and B.

Example 2

0.304g of a Norton Company Crystolon™ SiC powder with a specific surface area of 15 m²/g was spread on disc of high purity graphite crucible and placed in an Astro Industries, Inc. (Santa Barbara, California) graphite resistance-heated high temperature furnace. The furnace was pumped down to primary vacuum using a rotary mechanical pump, and heated from 1000°C to 1700°C in about 1.5 hour, then held at 1690-1700°C for 11 hours. Upon cooling, a black powder was observed on the surface of the sample whereas the powder was beige before heat treatment, as shown in FIG. 2. Beige powder was observed underneath the black powder after the heat treatment as well. The weight loss of the powder was measured to be 45.7%, indicating partial conversion of the SiC to carbon overall. (Full conversion has an ideal weight loss of 70%). The black surface powder was removed and studied further. X-ray diffraction of this material showed sharp diffraction peaks for 6H-SiC, along with a broad peak at ~36.3° where graphite has its strongest peak. The breadth of this peak was consistent with the presence of fullerenic carbon.

High resolution electron microscopy (HREM) was performed on this sample. An exemplary particle was ~0.7 micrometer in breadth and ~2.5 micrometer in length and consisted almost entirely of fullerenic carbon in the form of multiwalled nanotubes. The corresponding electron diffraction pattern shows that some crystallographic texture of the nanotubes exists within the particle. Higher magnification images showed arrays of carbon nanotubes in the sample. This example shows that particles of a silicon carbide powder can be completely converted to fullerenic particles through thermochemical treatment. These results demonstrate that volumetrically dense, bulk carbon nanotubes can be produced.

Example 3

0.127g of a Norton Company Crystolon™ SiC powder with a specific surface area of 15 m²/g was spread on disc of high purity graphite crucible and placed in an Astro Industries, Inc. (Santa Barbara, California) graphite resistance-heated high temperature furnace. The

furnace was pumped down to primary vacuum using a rotary mechanical pump, and heated from 1000°C to 1500°C in about 0.5 hour, then held at 1500°C for 14 hours. Upon cooling, a black powder was observed whereas the powder was beige before heat treatment. The weight loss of the powder was measured to be 13.4%, indicating less conversion of the SiC to carbon than in Example 2. Representative particles of about 0.1 to about 0.2 micrometer in diameter, respectively, showed that the entirety of the surface of the particle has been converted to carbon nanotubes, leaving in each instance a core of unconverted silicon carbide. The diameter of the carbon nanotubes ranged from 2-10 nm. This example shows that composite particles consisting of a fullerenic surface and silicon carbide core can be prepared by the thermochemical treatment of silicon carbide particles. Representative electron micrographs are shown in FIGS. 3A and 3B.

Example 4

0.084g of a Norton Company Crystolon™ SiC powder with a specific surface area of 15 m²/g was spread on disc of high purity graphite crucible and placed in an Astro Industries, Inc. (Santa Barbara, California) graphite resistance-heated high temperature furnace. The furnace was pumped down to primary vacuum using a rotary mechanical pump, and heated from 1000°C to 1700°C in about 0.5 hour, then held at 1700°C for 24 hours. The powder was found to have lost 63.8% weight, which indicated that it was 91% converted to carbon. X-ray diffraction of this material showed that the broad peak at 26.3° to be of much greater intensity relative to the diffraction peaks for 6H-SiC compared to those observed in Example 3, confirming the nearly complete conversion of this SiC powder to carbon nanotubes.

Example 5

The material of Example 4 was found to intercalate lithium readily when tested in standard electrochemical cells. A portion of the material was mixed with PVDF binder using γ-butyrolactone as a solvent, dried and pressed into a thin ¼" pellet and tested against a lithium metal counter electrode in a stainless-steel cell. A 1:1 by volume mixture of ethylene carbonate and diethylene carbonate electrolyte containing 1M LiPF₆ was used as the electrolyte, and a disk of Celgard™ as used as the separator. FIG. 4 shows the initial charge-discharge behavior of a cell cycled at a relatively high current rate of 60 mAh/g between 0.005-2V. Comparing these results to literature data for CVD or laser ablation produced carbon nanotubes, it is clear that the present materials show much less hysteresis between the

charge and discharge branches, indicating lower polarization or surface reaction barrier to insertion/removal of lithium. FIG. 5 shows the gravimetric charge capacity vs. cycle number at 20 mA/g and 60 mA/g current rates, showing excellent stability of the charge capacity over >20 cycles. The gravimetric charge capacity of our materials is comparable to previous reports for multiwalled carbon nanotubes. Although volumetric capacities were not reported in these publications, it is clear that the volumetric capacity is proportional to packaging density. Since our materials can be packed to at least several times the density of previous carbon nanotube materials, the volumetric capacity is correspondingly greater.

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

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WHAT IS CLAIMED IS:

1. A composite comprising a particle including a core including silicon carbide and a shell covering at least a portion of a surface of the core including fullerenic carbon.
2. The composite of claim 1 wherein the shell covers at least 50% of the surface.
3. The composite of claim 1 wherein the particle includes at least 2% by volume fullerenic carbon.
4. The composite of claim 1 wherein the shell has an average thickness of at least 2.5 nm.
5. The composite of claim 1 wherein the particle has an average diameter of less than 100 micrometers.
6. The composite of any of claim 1 wherein the fullerenic carbon is a single-walled or multi-walled carbon nanotube or a nanofiber chemically attached to the core of silicon carbide at least one end.
7. The composite of claim 1 wherein the fullerenic carbon is a carbon nanotube or carbon nanofiber open at an end not attached to the core.
8. A method of manufacturing an article including fullerenic carbon on a surface of the article comprising:
 - heating the article including a metal carbide in a first atmosphere for a period of time to generate fullerenic carbon nuclei on the surface of the article, the first atmosphere being a reducing atmosphere relative to the metal carbide; and
 - heating the article including fullerenic carbon nuclei in a second atmosphere to grow the fullerenic carbon on the surface of the article.
9. The method of claim 8 wherein the metal carbide includes silicon carbide.
10. The method of claim 9 wherein the silicon carbide is cubic or beta silicon carbide powder, or hexagonal or alpha silicon carbide powder.
11. The method of claim 8 further comprising providing a carbon source for growing the fullerenic carbon.
12. The method of claim 11 wherein the carbon source is not silicon carbide.

13. The method of claim 8 wherein heating the article including the metal carbide in the first atmosphere includes heating the article at a pressure of greater than 10^{-3} Torr.

14. The method of claim 13 wherein heating the article including the metal carbide in the first atmosphere includes heating powder at a temperature between 1200°C and 2000°C.

15. A method of manufacturing fullerenic carbon comprising:
heating silicon carbide in an oxygen-containing gas atmosphere and at a temperature in which silicon carbide is in the active oxidation regime and carbon is in the graphite stability regime.

16. The method of claim 15 wherein the gas atmosphere supplied to the silicon carbide is CO or a mixture of CO and CO₂ and the temperature is in the range 1000°C to 2000°C.

17. A method of manufacturing fullerenic carbon comprising:
heating silicon carbide in an inert gas atmosphere at a temperature between 1200°C and 2000°C.

18. The method of claim 17 wherein the inert gas includes helium.

19. The method of claim 17 wherein the inert gas includes hydrogen.

20. The method of claim 17 wherein the inert gas is a nitrogen-hydrogen mixture.

21. The method of claim 17 wherein the inert gas includes argon.

22. The method of claim 17 further comprising heating the silicon carbide to nucleate the fullerenic carbon prior to heating the silicon carbide in an inert gas atmosphere at a temperature between 1200°C and 2000°C.

23. A composite abrasive particle comprising a silicon carbide core and a fullerenic outer shell.

24. An abrasive particle comprising substantially densely-packed fullerenic carbon.

25. The abrasive particle of claim 23 further comprising a coating of metal oxide or metal over the fullerenic carbon.

26. The abrasive particle of claim 24 further comprising a metal oxide or metal infiltrating the fullerenic carbon.

27. A grinding or finishing product comprising a particle of claim 1 or 24.

28. The grinding or finishing product of claim 27 wherein the product is a grinding wheel, cutting wheel, coated abrasive, or suspension of abrasive particles in a liquid.

29. A structurally reinforced composite comprising a particle of claim 1 or 24 contained in a matrix.

30. An electrochemical storage medium comprising a particle of claim 1 or 24.

31. A hydrogen storage medium comprising a particle of claim 1 or 24.

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ABSTRACT

Carbide powders can be partially or completely converted to substantially densely-packed carbon nanotubes by thermochemical treatment. When partially converted, the resulting materials can consist of a metal carbide core, such as silicon carbide, onto which a surface layer of fullerenic carbon, such as carbon nanotubes, has been grown.

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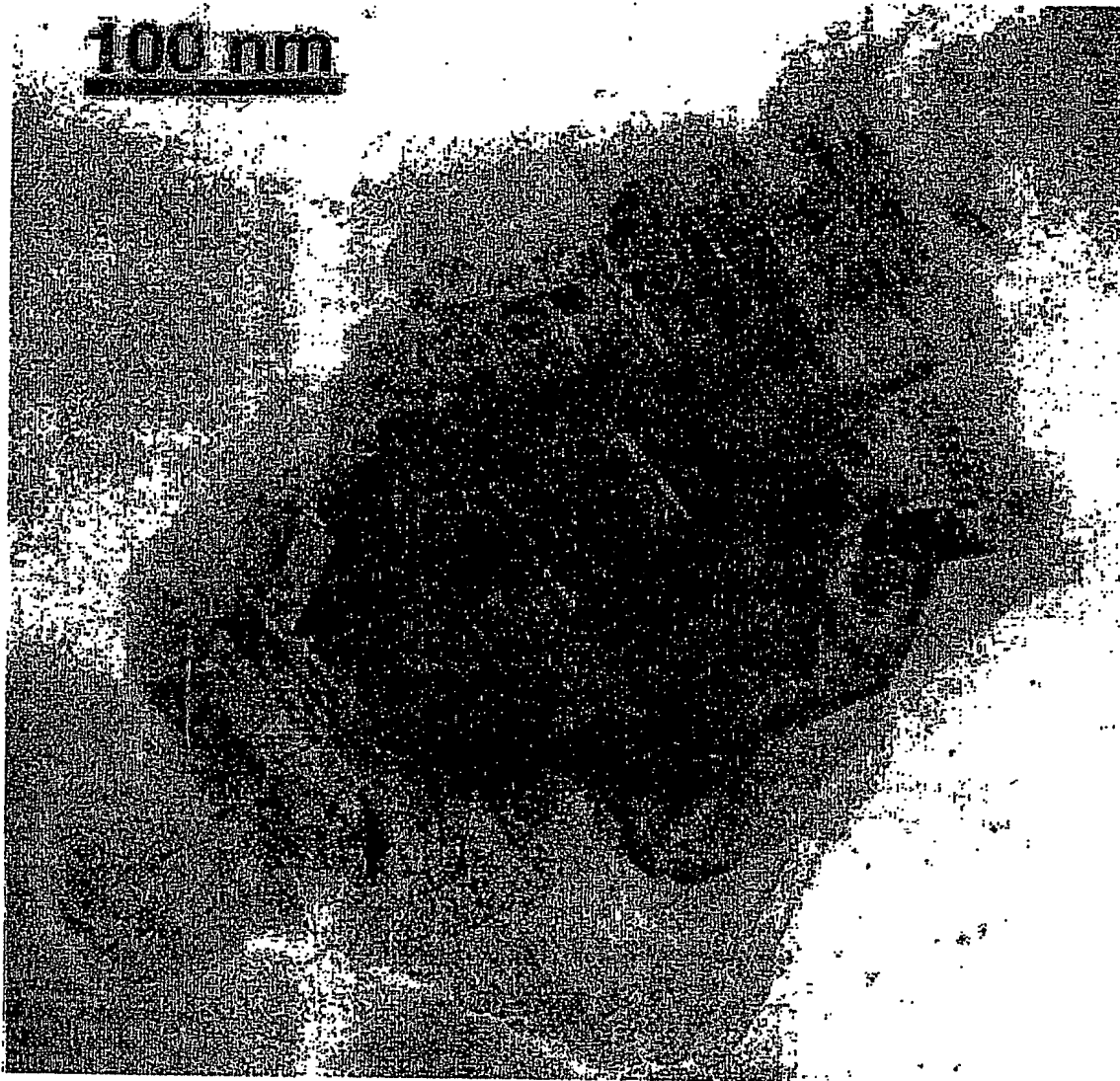


FIG 1A

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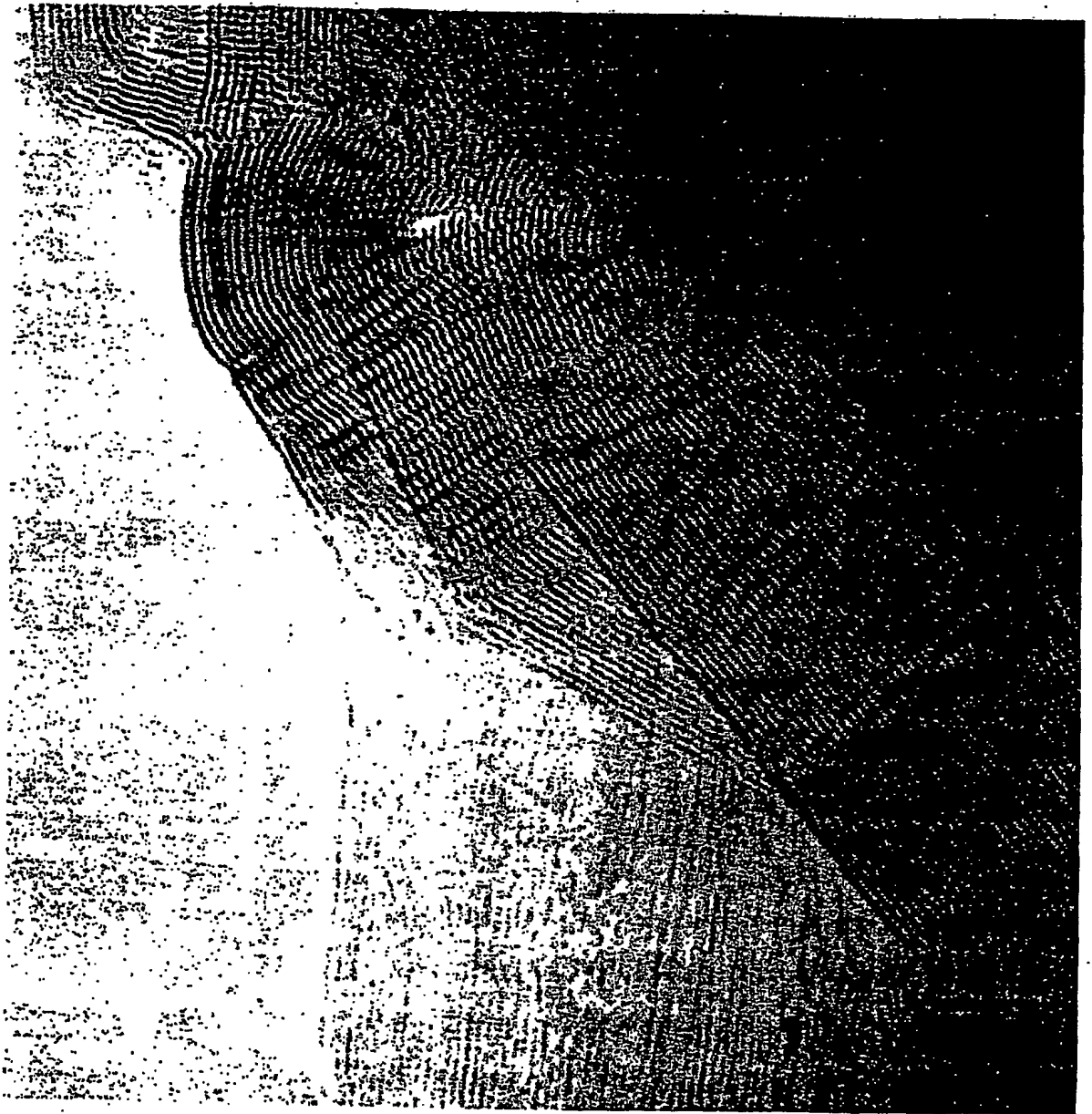


FIG. 1B

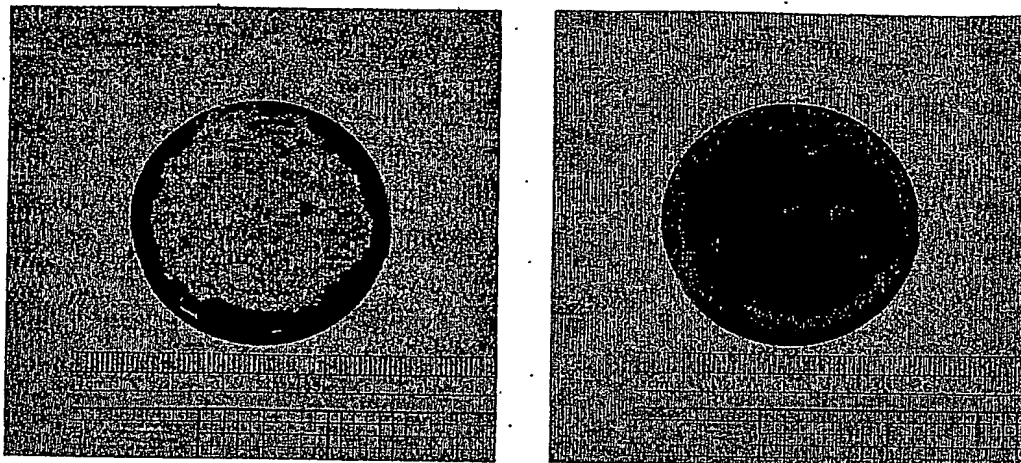


FIG 2

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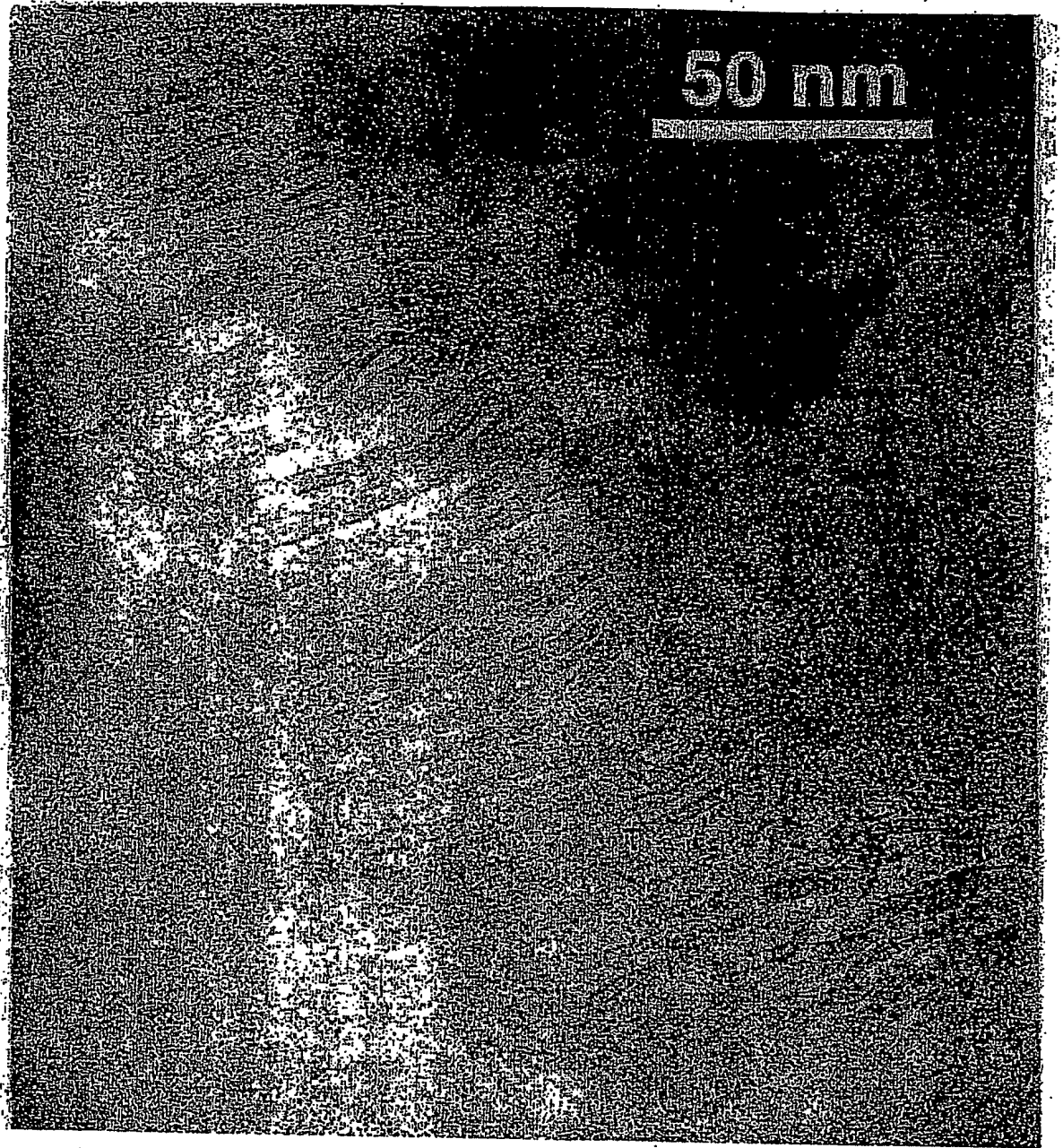


FIG 3B

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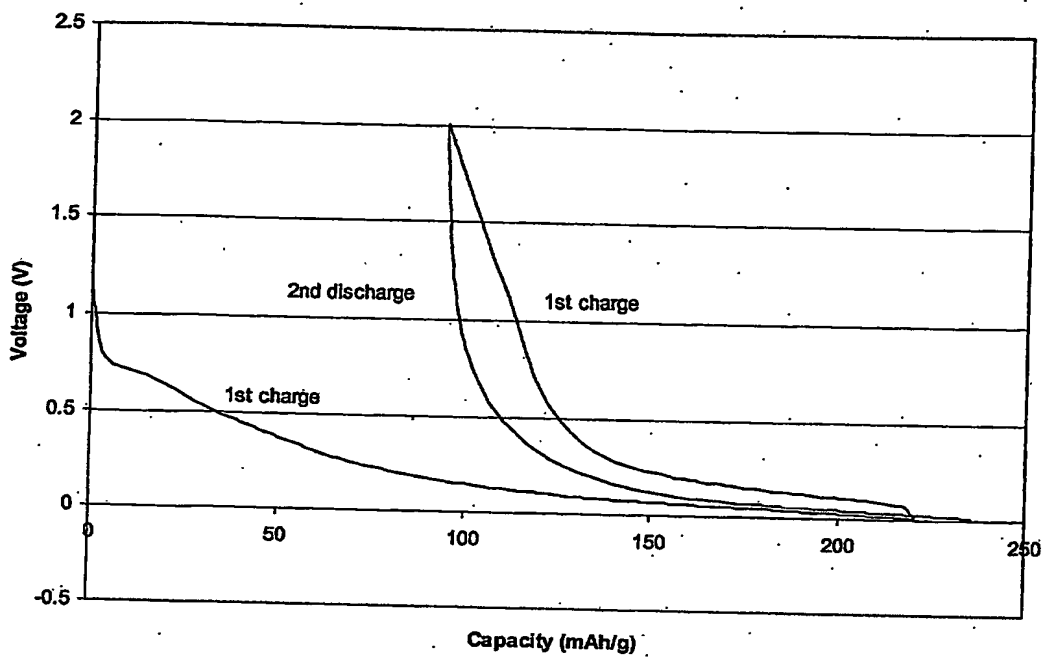


FIG. 4

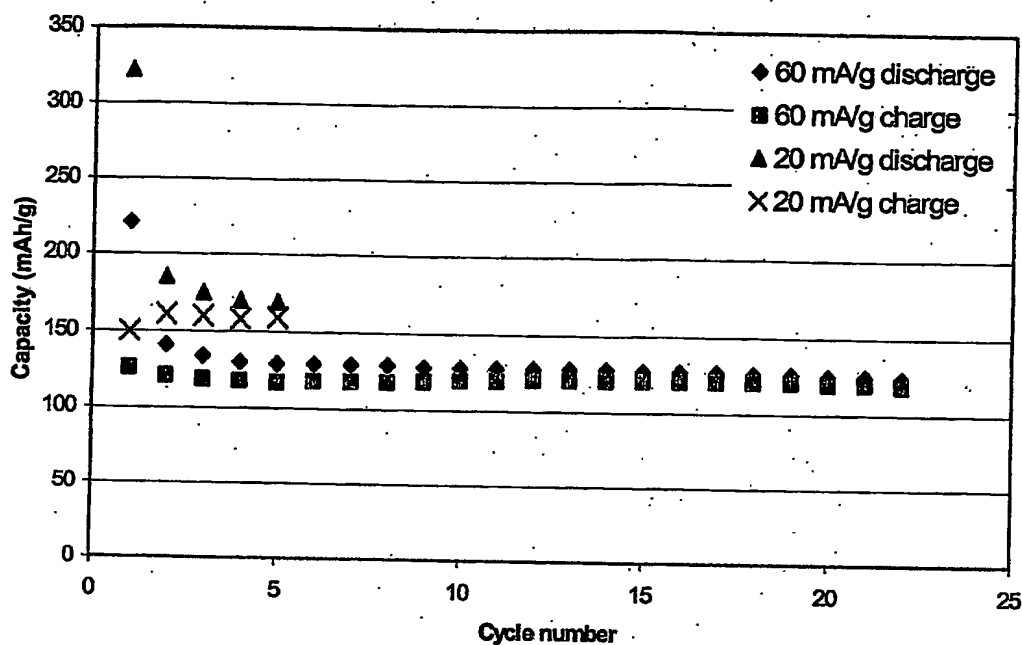


FIG. 5

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